New Polymeric Proton Conductors for High Temperature Applications

John Kerr, Xiao-Guang Sun, Gao Liu,
Jiangbing Xie and Craig Reeder
Lawrence Berkeley National Laboratory,
MS 62R0203, 1 Cyclotron Road,
Berkeley CA, 94720
jbkerr@lbl.gov

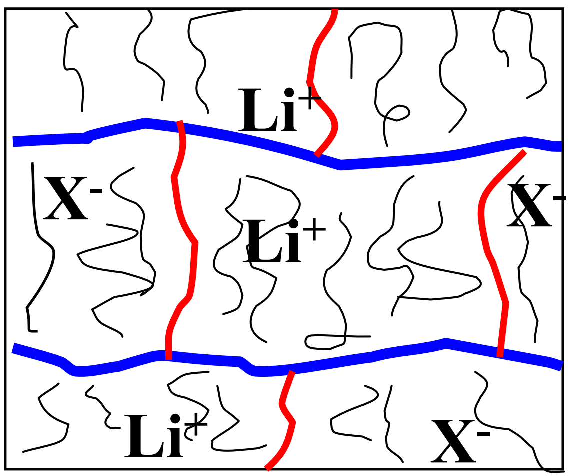
Outline

- Background
  - Solid Polymer vs. Gel Polymer Ion Transport
  - Lithium ion transport vs. Proton transport.
  - Common features for Lithium Polymer batteries and PEMFC’s.
- Polymer design & Synthesis.
- Preliminary Results
- Future schedule and testing development

Liquids vs. Gels vs. Dry Polymers
Transport mechanisms differ

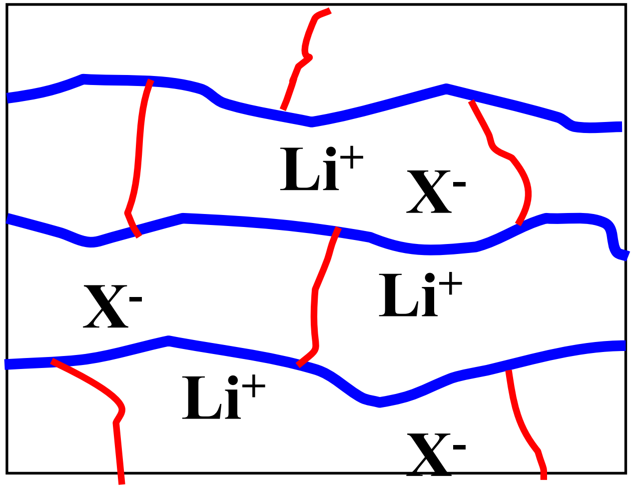
(blue: polymer chain; red: cross-linker; black: solvent)

Gel Polymer – Li Ion and Fuel Cell



Network Backbone may be polymer or inorganic. Free liquid moves with ions. Operates at ambient temp.

Dry Polymer – Li Metal/polymer & Fuel Cells –High Temp PEM (150^{0}C)

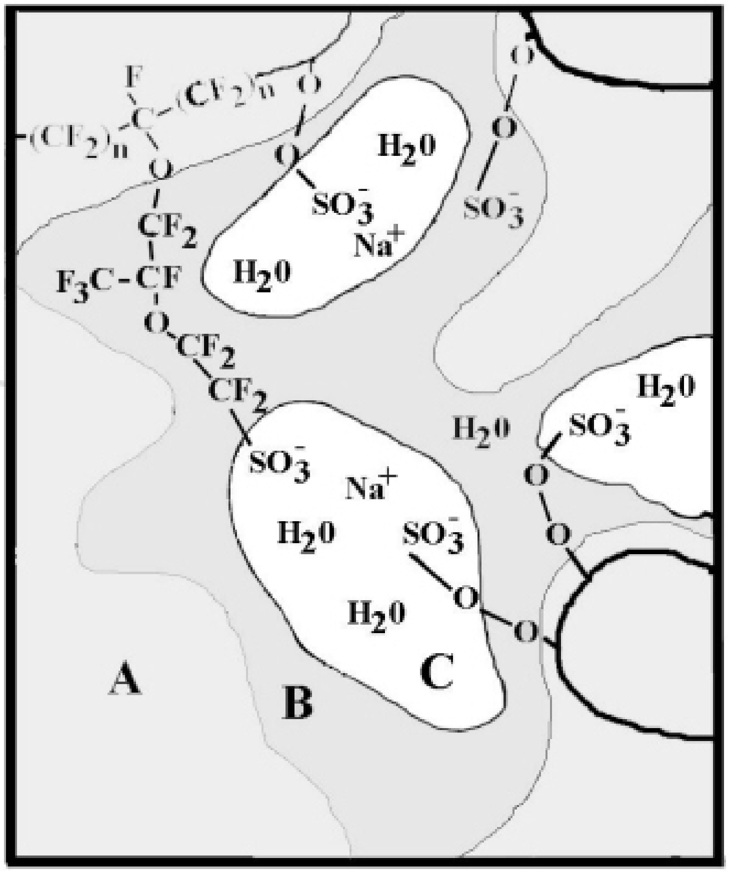


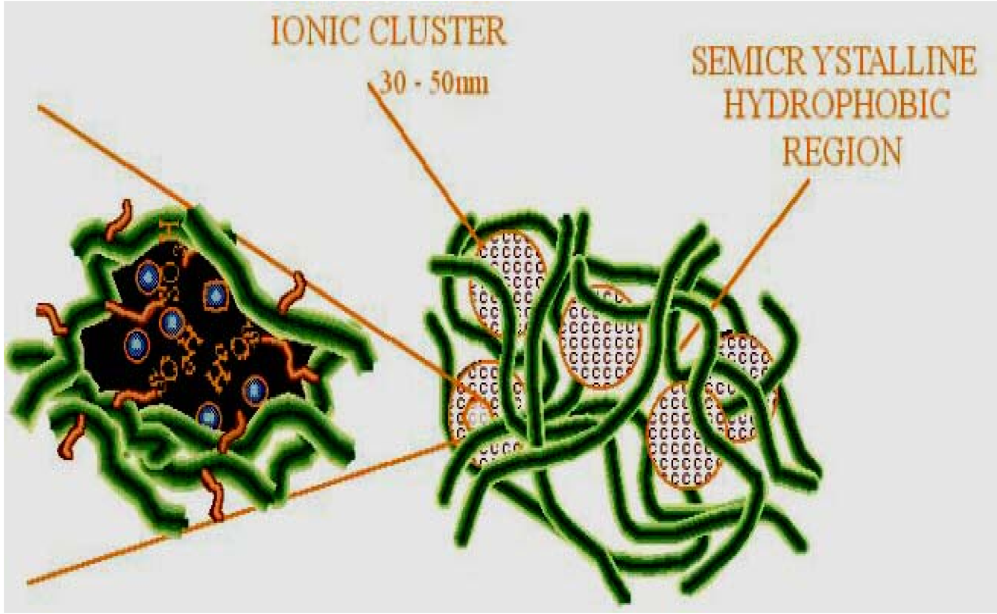
One or both ions are solvated by polymer. Ions move due to segmental motion of polymer. Need 85^{0}C for EV performance

Anions may be tethered to polymer backbone by means of side chains. Molecular structure determines morphology and properties.

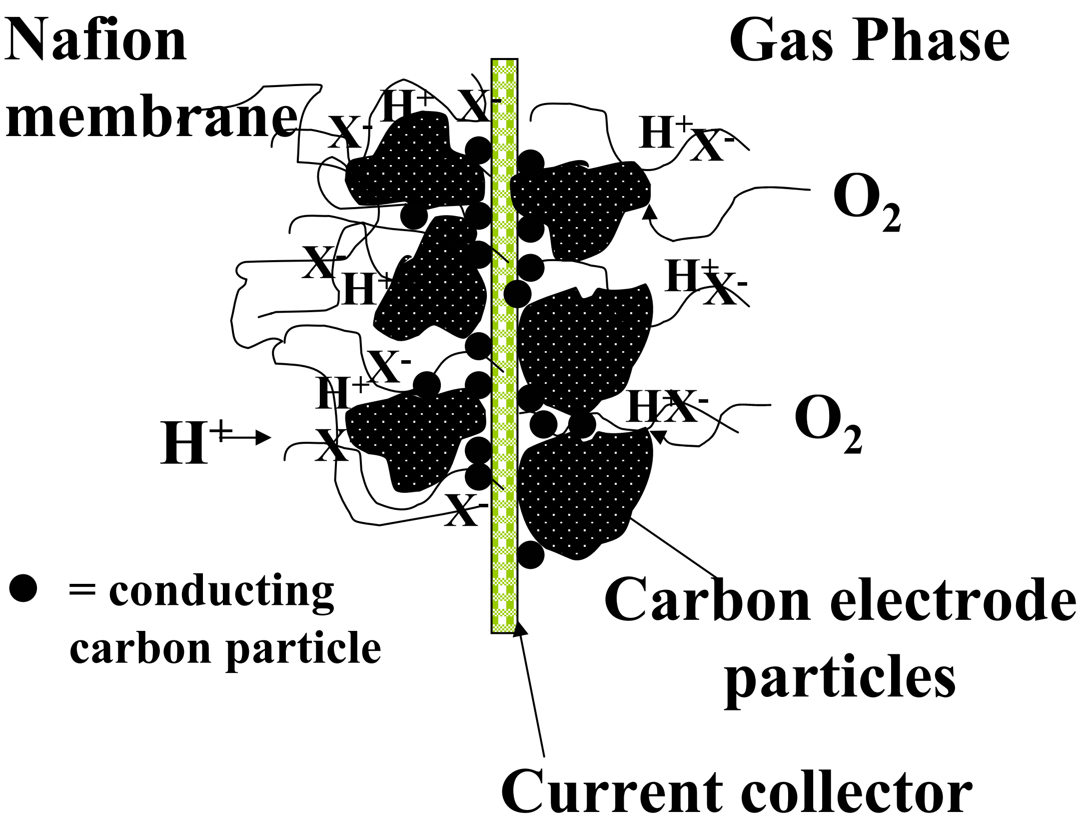
Fuel Cell Membranes
Microscopic to Macroscopic

Anions tethered to polymer. Cations (H^+, Na^+) are mobile and solvated by water.
Molecular structure determines morphology and formation of ionic, water-rich clusters.





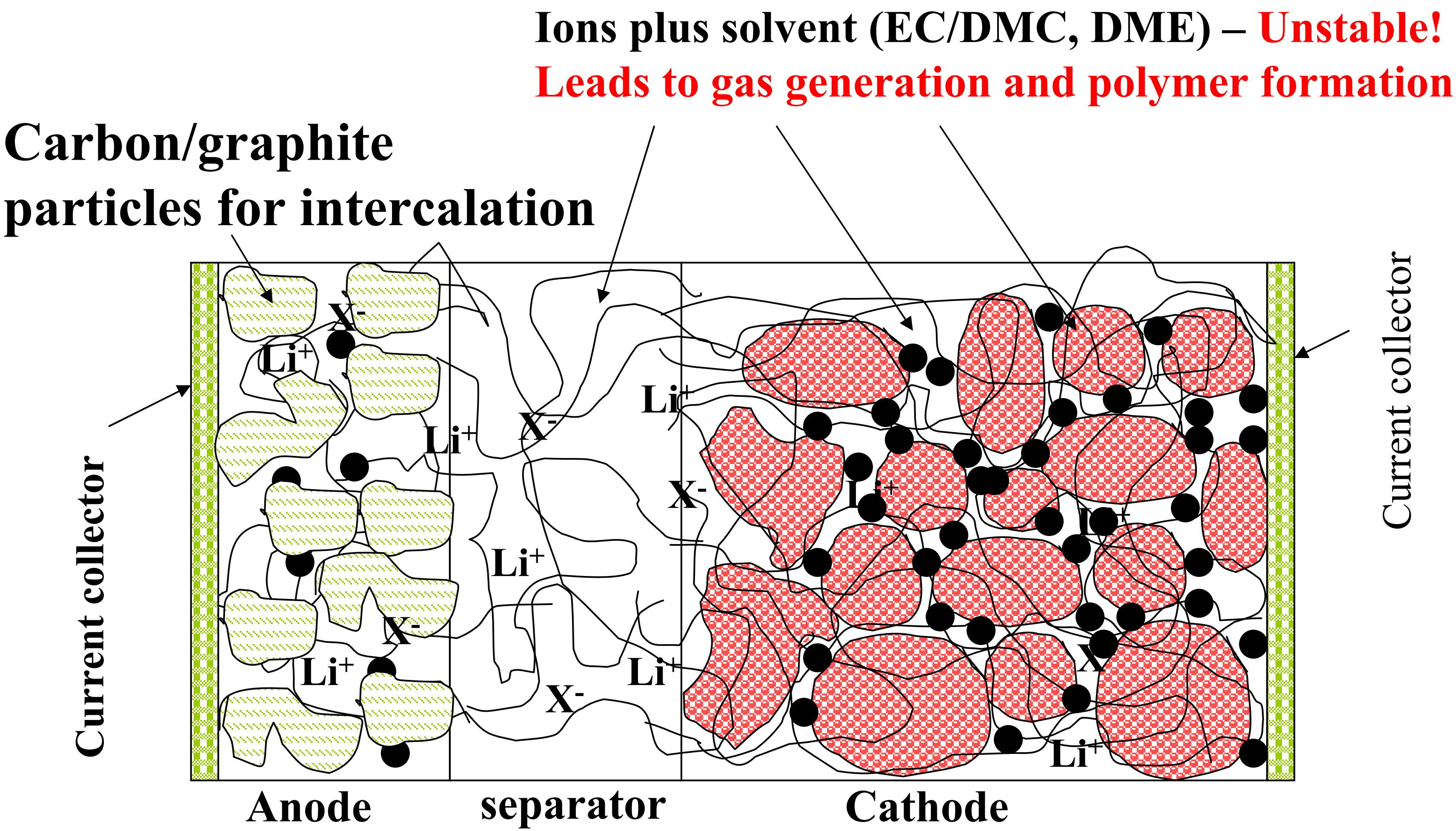
Fuel Cell Composite Electrodes.



- Transport of gases and ions through crowded polymer-solid interfaces where the electrolyte mobility is restricted.
- Polyelectrolytes close to glassy phase in presence of electrode surfaces.
- Poor ion transport and dis-bondment.
- Ion activity?

Composite Electrodes in Li Ion Cells

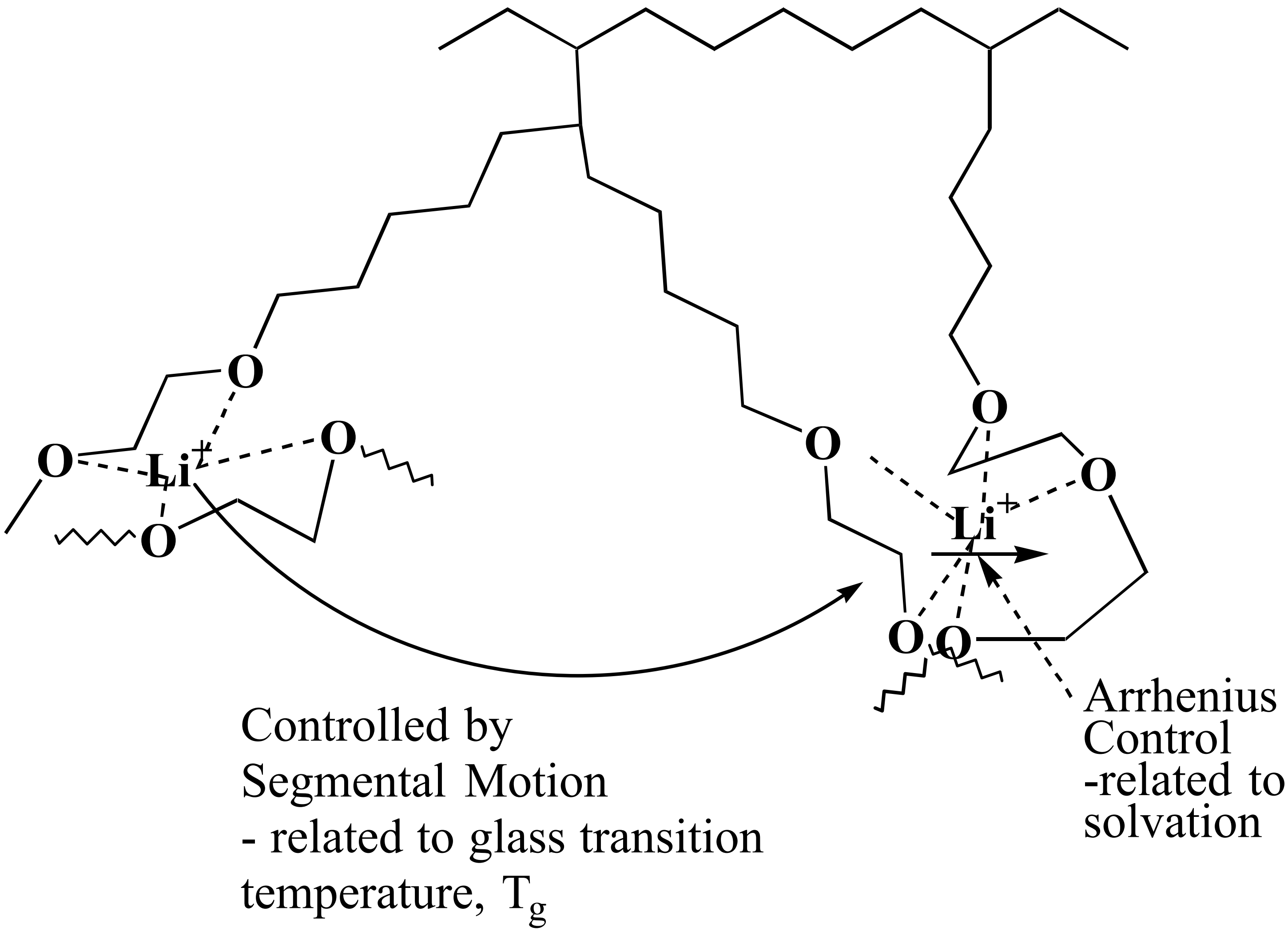
Lithium ions in crowded neighborhoods



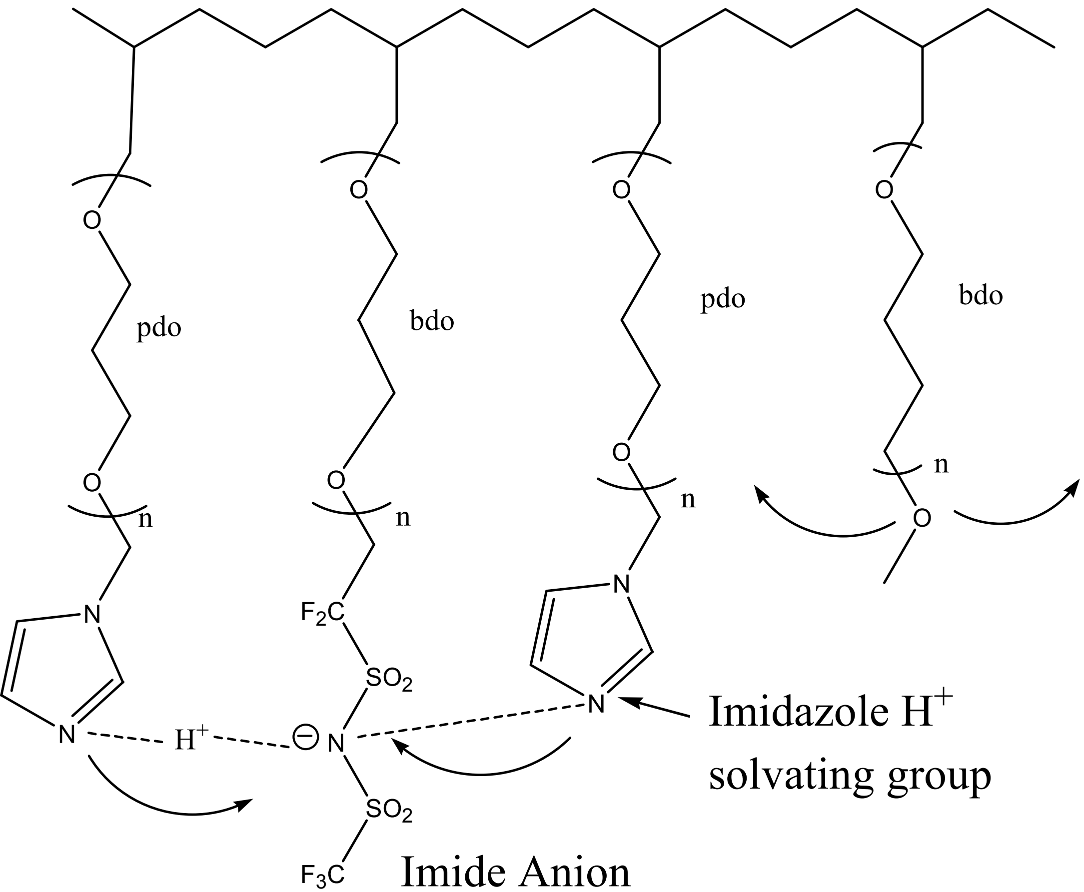
● = Conducting carbon particle

= cathode particle

Mechanisms of Ion Mobility in “Dry” Polymers - Amorphous Phase

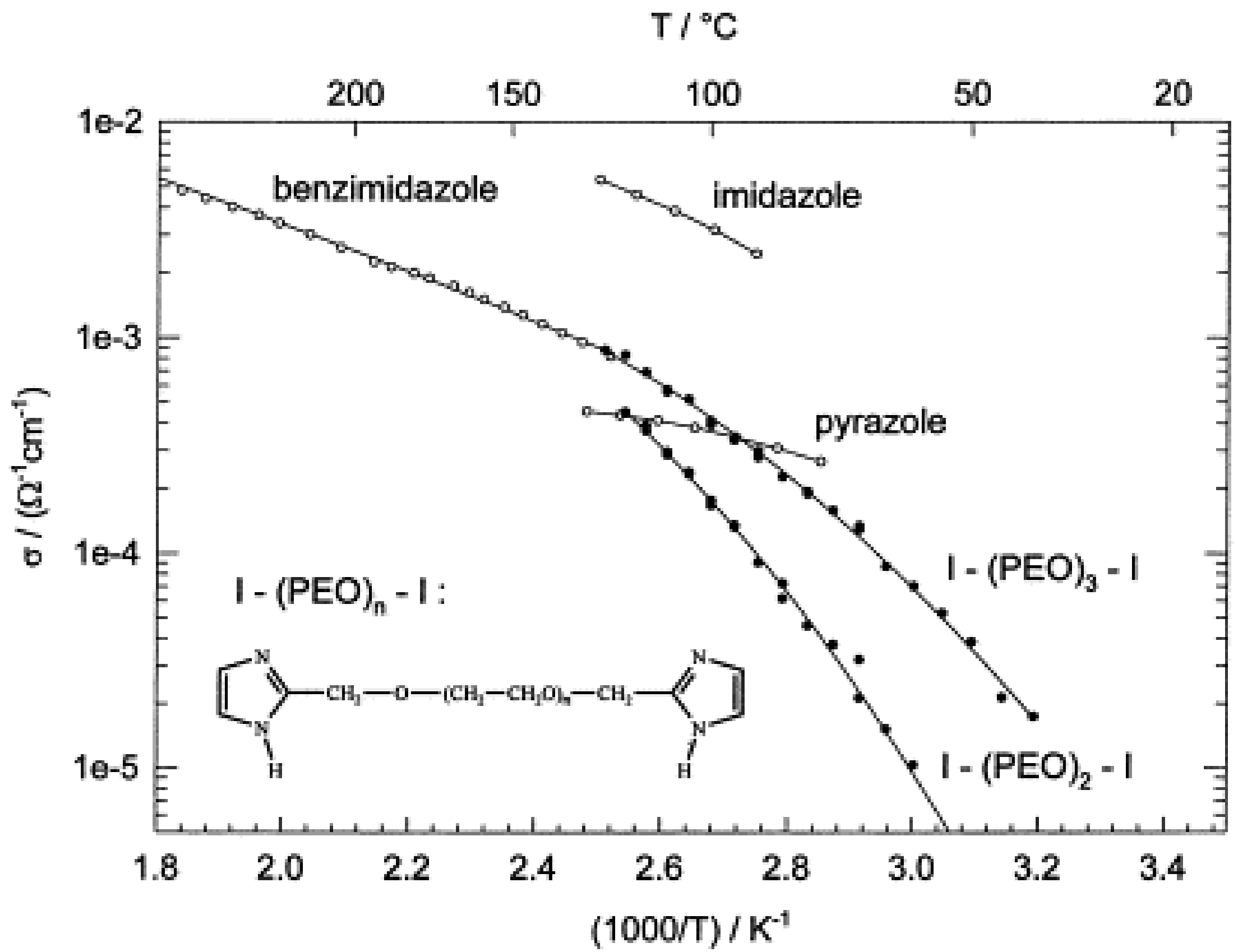


New Polymer Architectures for Imidazole Solvating groups, Anion Mobility and Flexibility

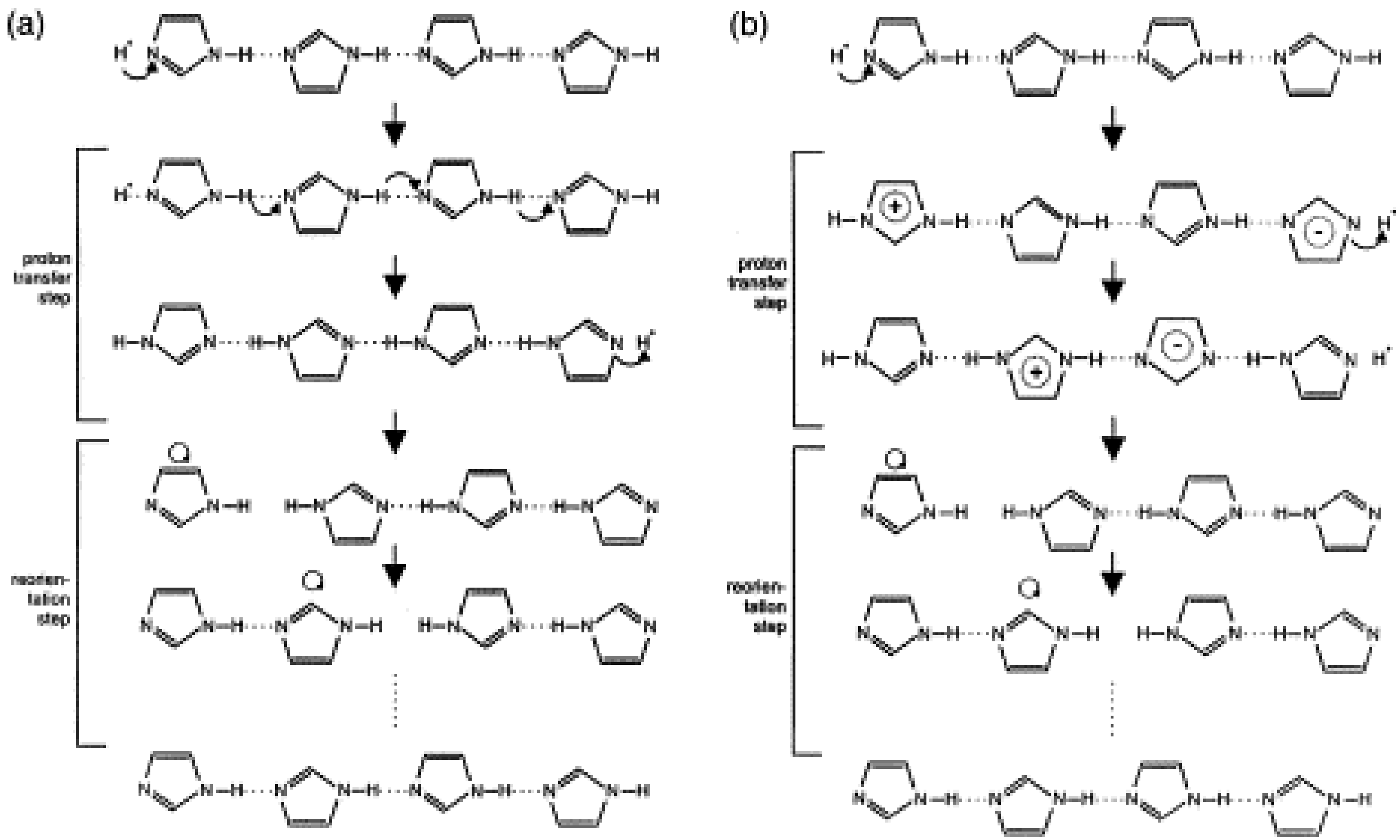


- Attach anions and solvating groups by grafting –control nature and concentration.
- Use nature (pdo/bdo) and length of side chain to control chain mobility.
- Backbone (PE, polystyrene, polysiloxane) and cross-link density to control mechanical & morphological properties.
- Degradation results in Release of small fragments - facilitates failure analysis.

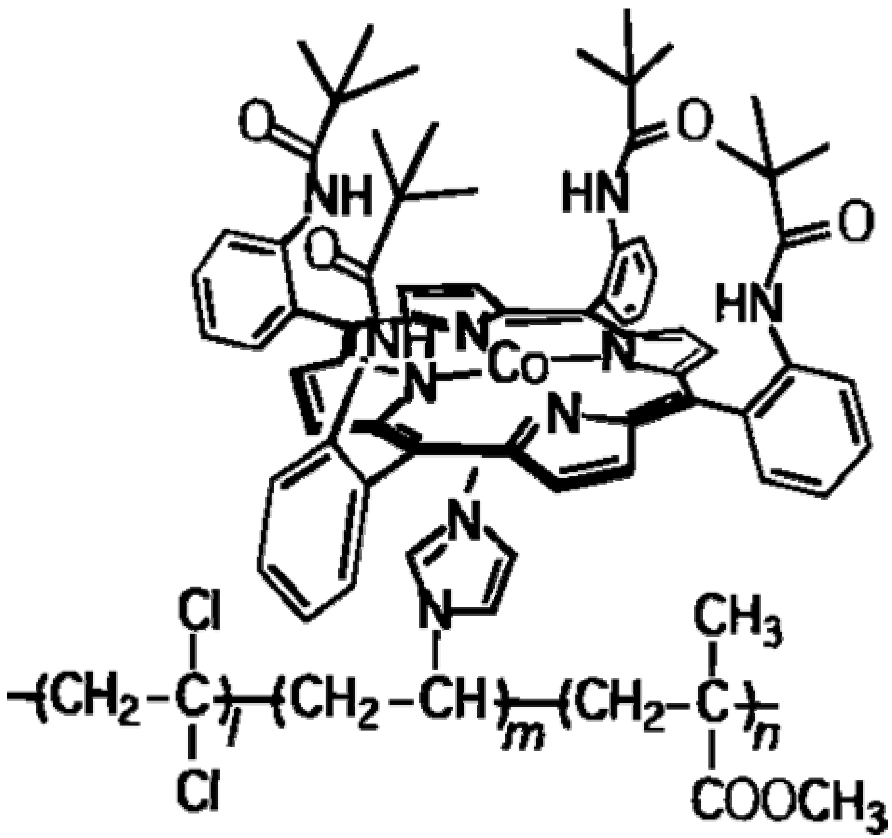
Imidazole Proton Conductivity



Grotthus Proton Transfer?



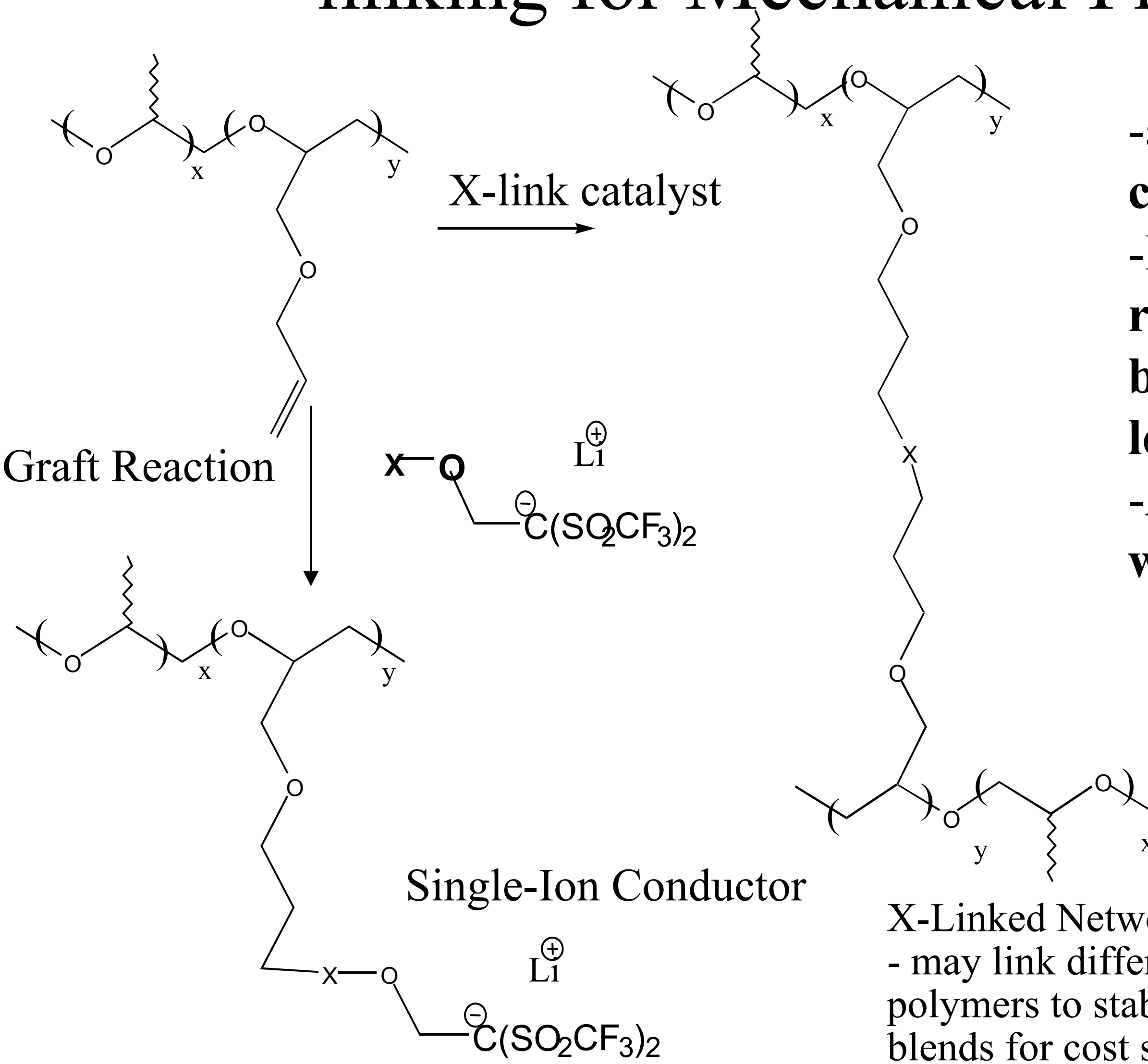
Oxygen Separation Membrane exhibits stability to (per)oxygen



- Vinyl Imidazole used rather than vinyl pyridine.
- PolyvinylImidazole has high T_g. Membrane is very selective for O_2 over N_2.

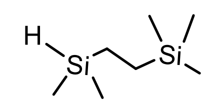
Hiroyuki Nishide,* Yukihiro Tsukahara, and Eishun Tsuchida,
J. Phys. Chem. B, 102 (44), 8766 -8770, 1998.

Hydrosilylation Chemistry Allows Grafting of Functions (Anions or Imidazoles) and Cross-linking for Mechanical Properties.

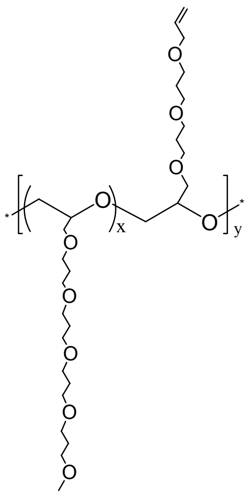


-allyl groups are reactive centers in this chemistry.
-Hydrosilation is reproducible, provides better uniformity and leaves no residues.
-Allyl groups do not react with radical initiators

X =



Prepolymers and Salts

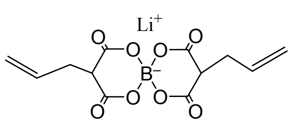


Prepolymer

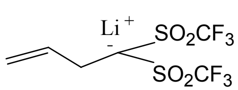
CH2=CH-CH2-O-CF2-CFH-O-CF2-CF2-SO2N(Li)SO2CF3

CH2=CH-CH2-O-CF2-CFH-O-CF2-CF2-SO3(Li)

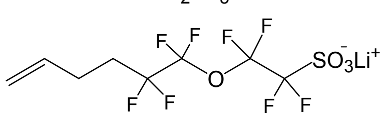
New salts arriving from DesMarteau Group (Clemson)



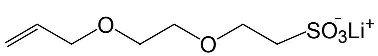
Salt I



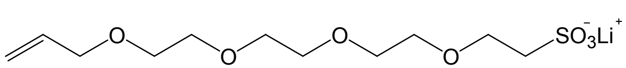
Salt II



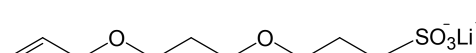
Salt III



Salt IV

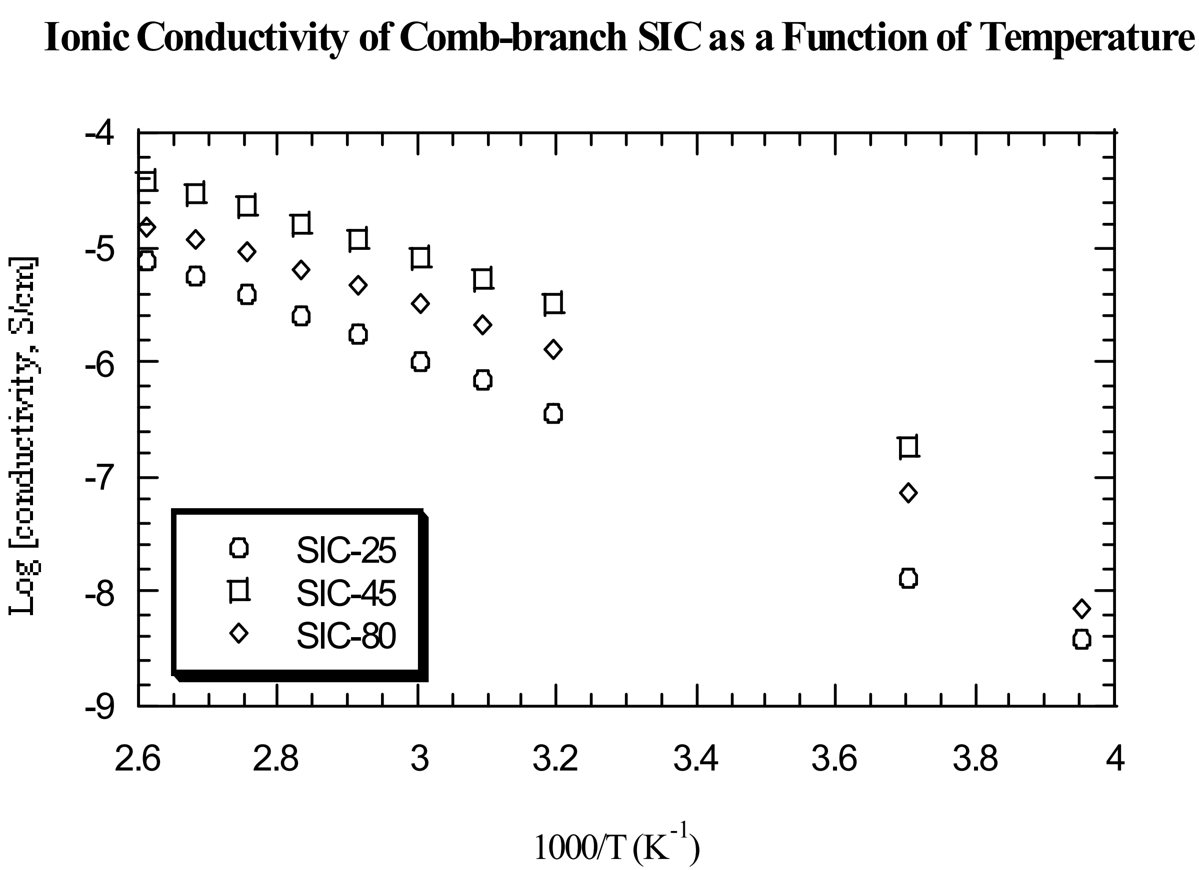


Salt V



Salt VI

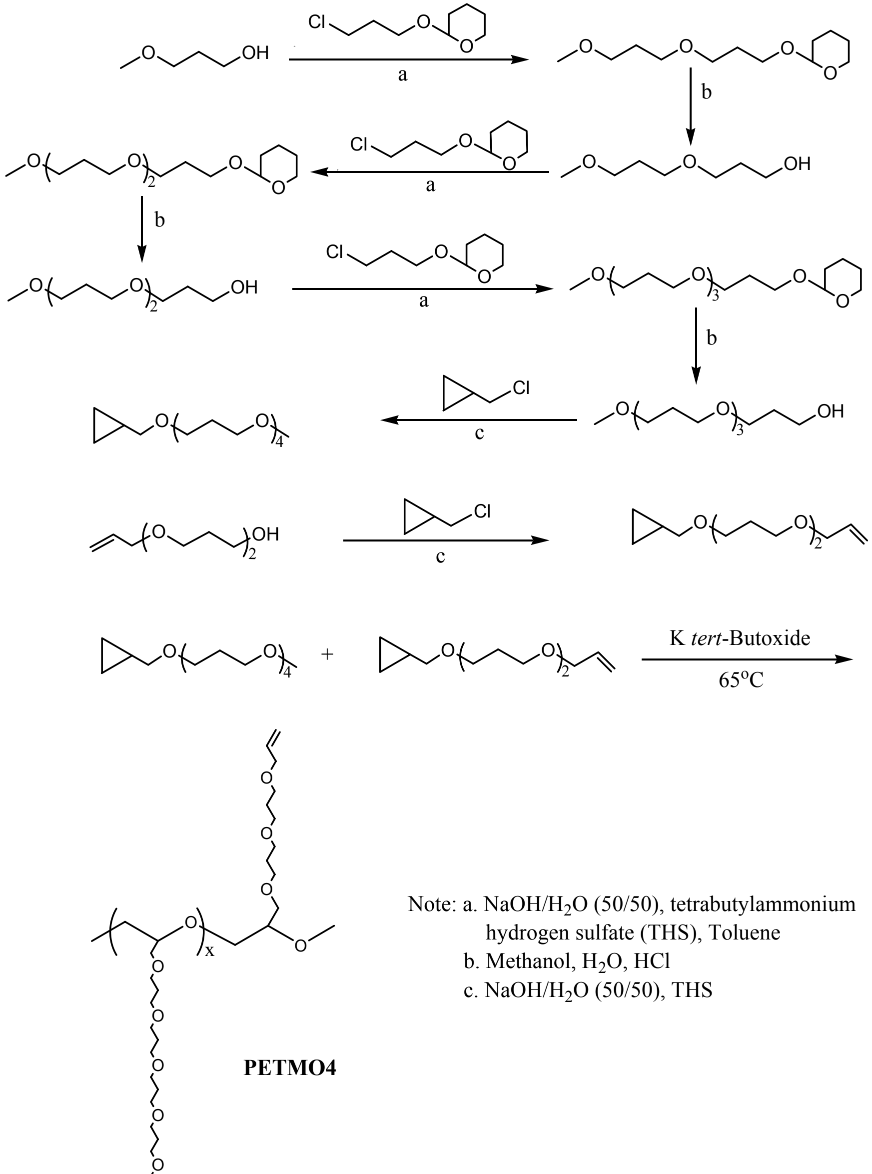
Conductivity of Li^+ Polyelectrolytes

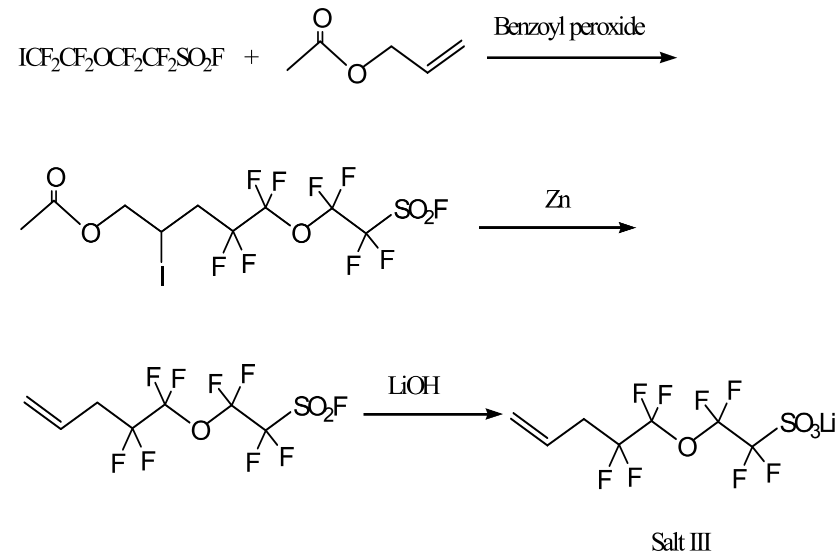


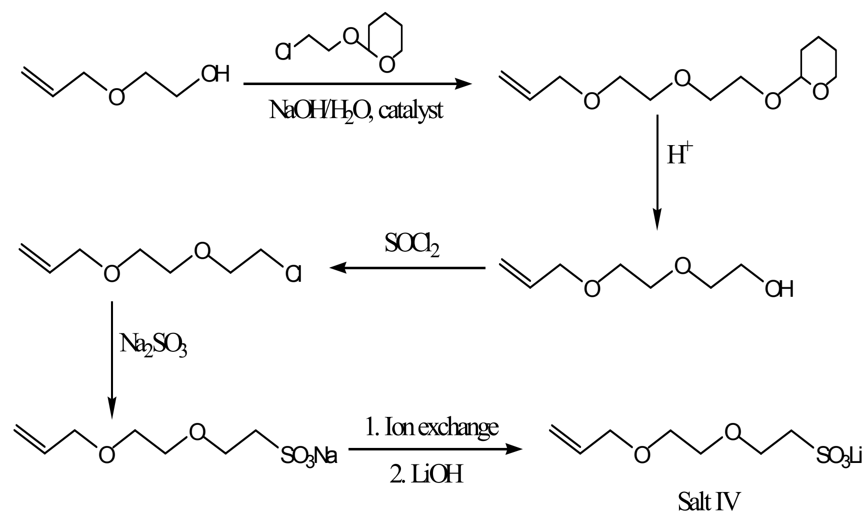
T_g: 80 = -54°C; 45 = -53°C; 25 = -35°C

- Theoretical models predict optimum ion concentration to be half the optimum for binary salts. (Ratner JES 148, A858 (2001))
- Low salt concn. gives lower cost pathway.
- Lower T_g at higher ion concn. wanted for high conductivity.
- Side chain lengths and flexibility not optimized.

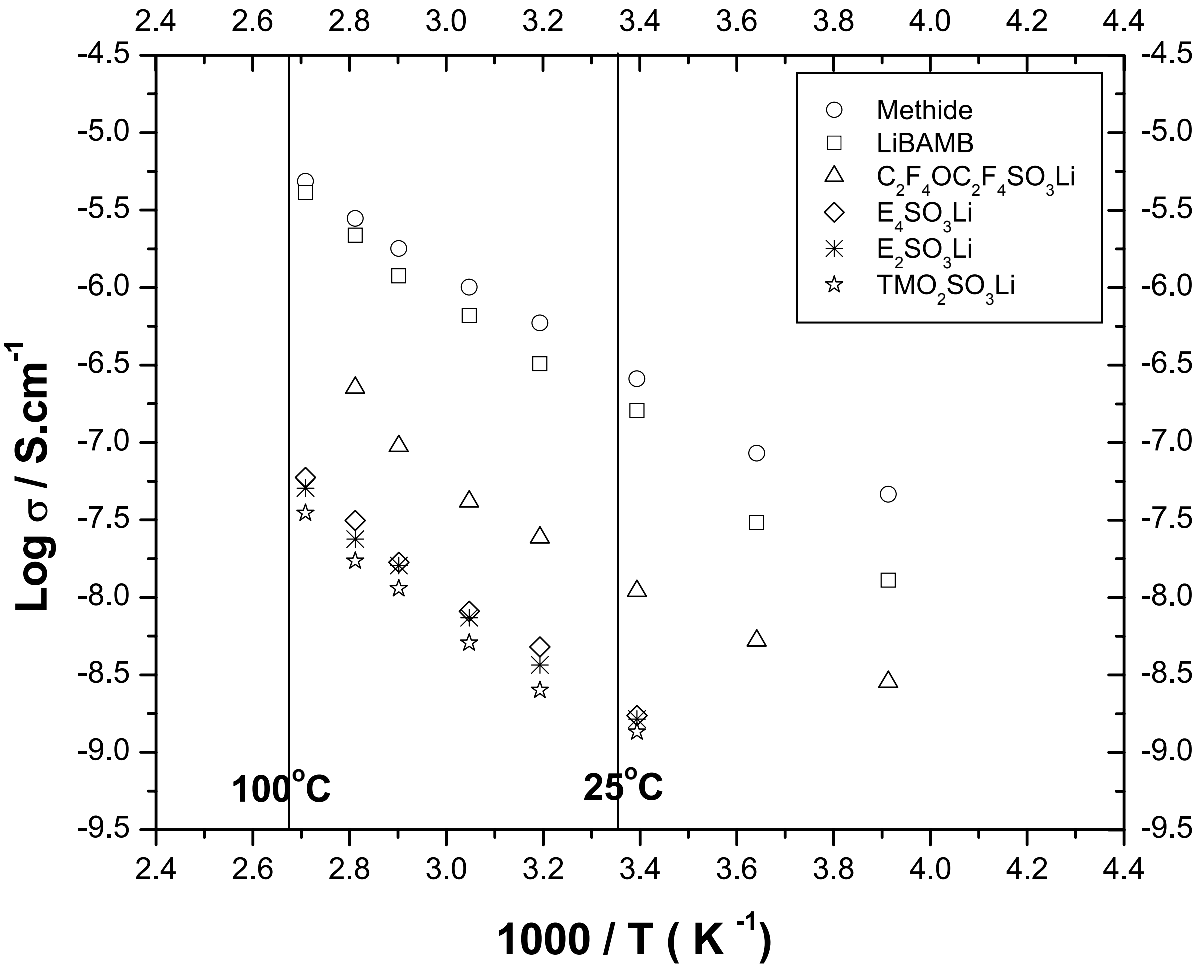
Synthesis of Prepolymers & Salts







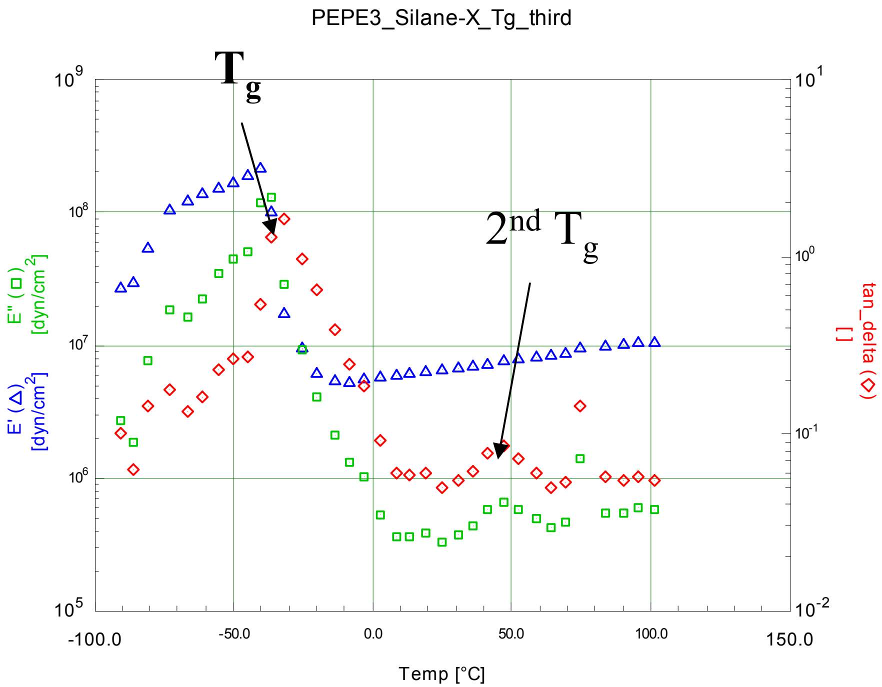
Conductivities of Lithium Polyelectrolytes

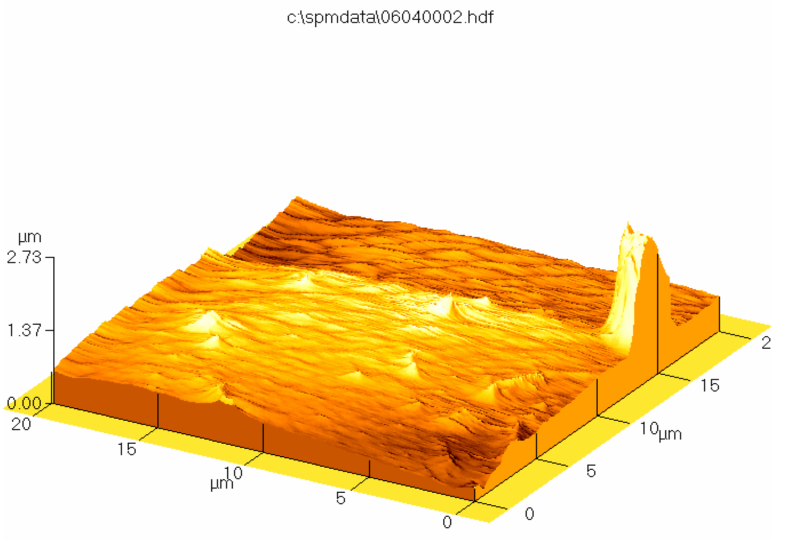


DSC results of PETMO4 based single ion conductors

Prepolymer	Salt	O/Li	$T_g/^oC$
$PETMO_4$-20	---	0	-85.66
$PETMO_4$-20	LiBAMB	48	-78.53
$PETMO_4$-40	----	0	-86.77
$PETMO_4$-40	E_2SO_3Li	54	-79.07
$PETMO_4$-40	E_4SO_3Li	56	-78.72
$PETMO_4$-40	TMO_2SO_3Li	54	-79.59
$PETMO_4$-40	Methide	52	-78.06
$PETMO_4$-40	$C_2F_4OC_2F_4SO_3Li$	54	-79.01

Uniformity of the Membrane is Critical! Rheology(DMTA) and AFM probe Membrane Properties and Uniformity – $PEPE_3$+ 10% AGE



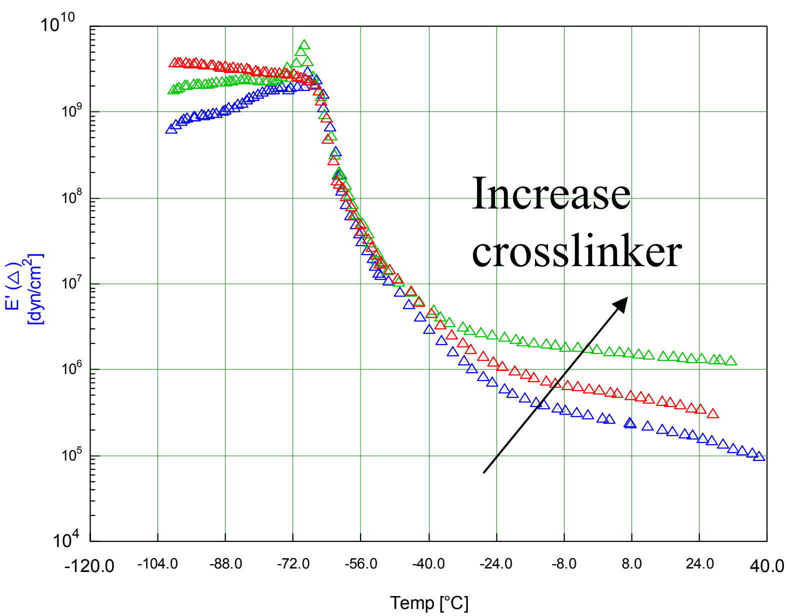


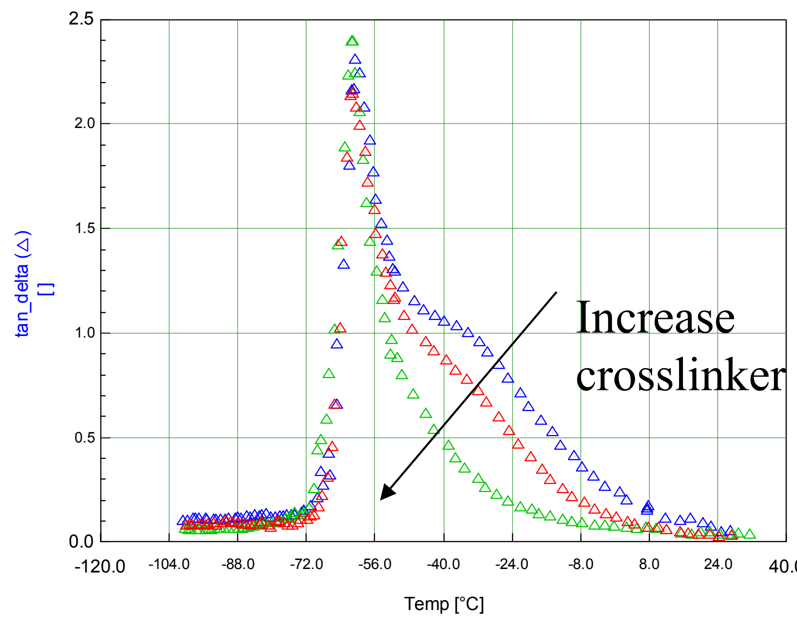
Rapid growth of dendrites observed in Li/Li cells

– due to thick membrane (400µm), high x-link density that degrades transport properties and non-uniformity from non-random polymer

Comb Structures allow Increase of Mechanical strength without Loss of Ion transport Properties?

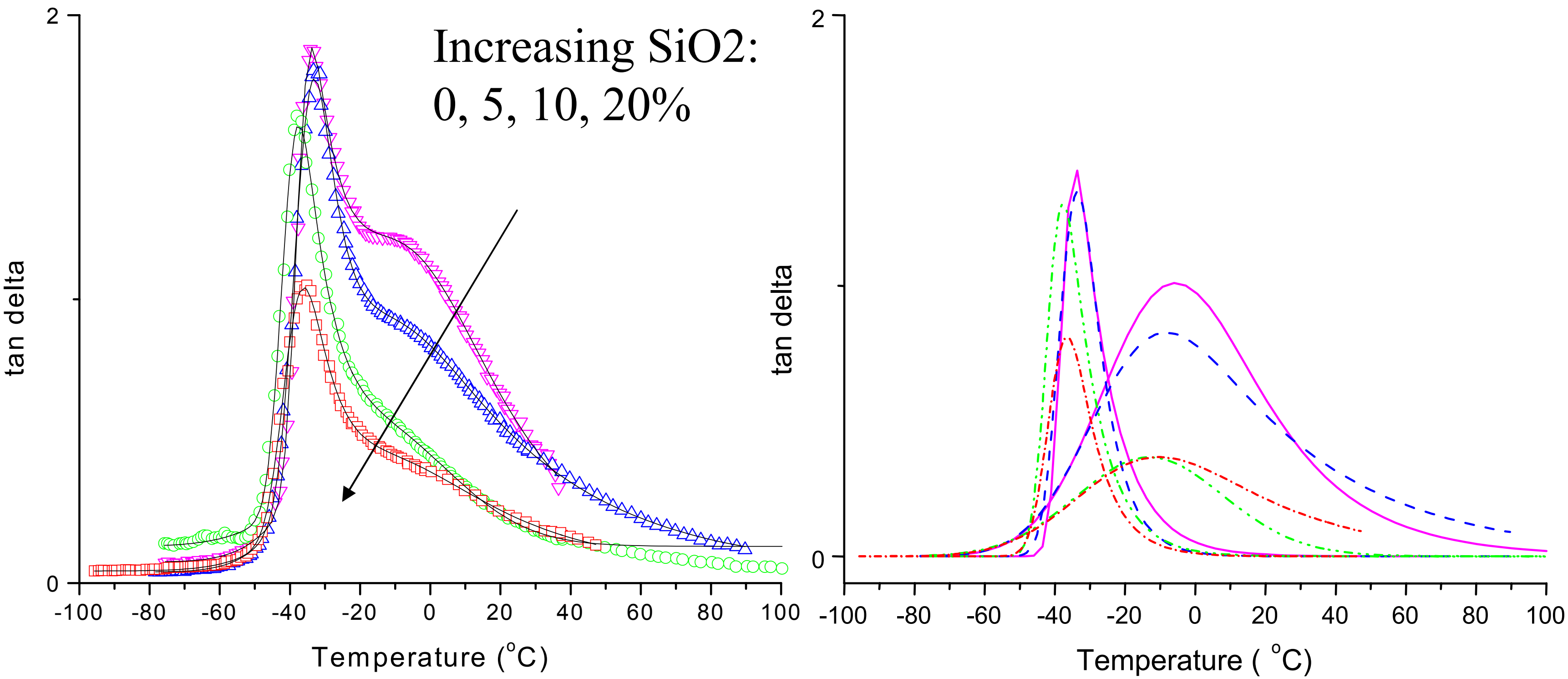
$PEPE_3$ (no salt) with different amount of crosslinker





Increase of X-link agent leaves fewer free allyl groups available to alter polymer morphology

PEPE3/LiTFSI 20:1 with different amounts of hydrophobic SiO_2 R805 filler

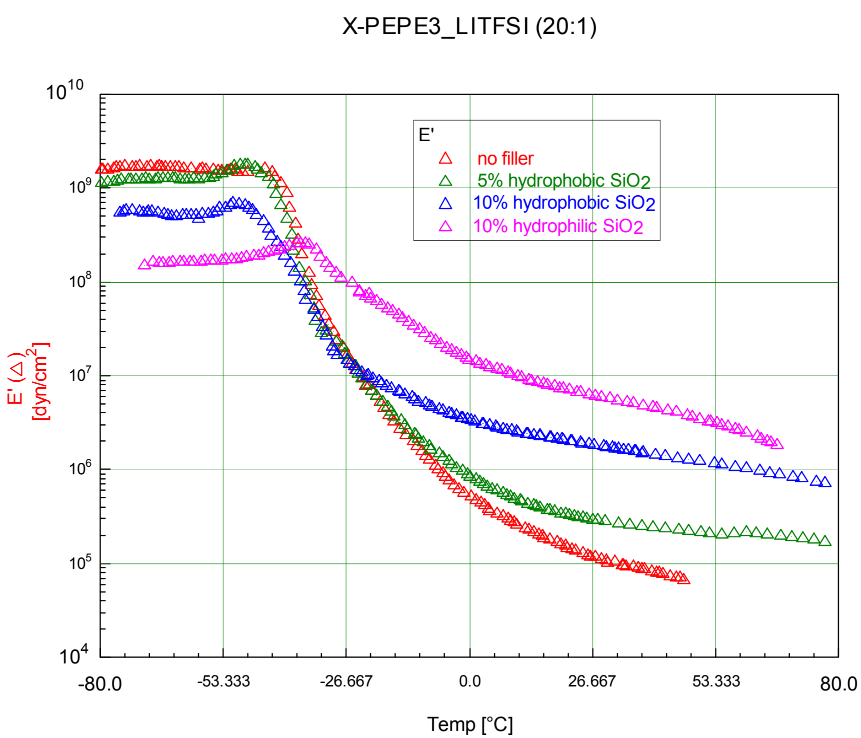


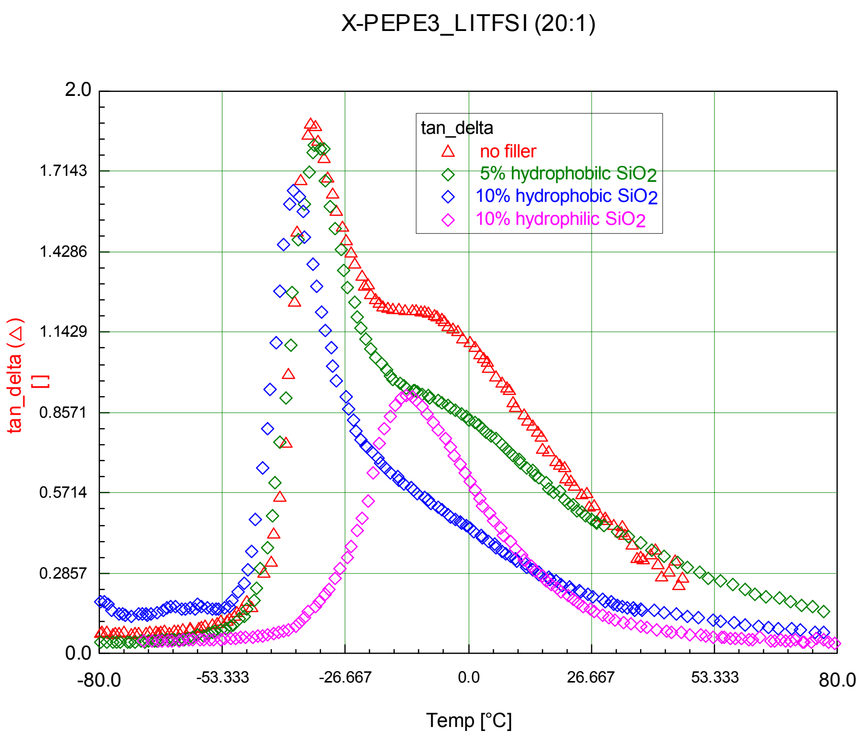
Combine X-link Chemistry with fillers for Increased Mechanical Properties

Different Surface Interactions influence Polymer Mobility (Temperature Sweep in Compression (10Hz))

Fumed SiO_2 -A200 –OH hydrophilic groups

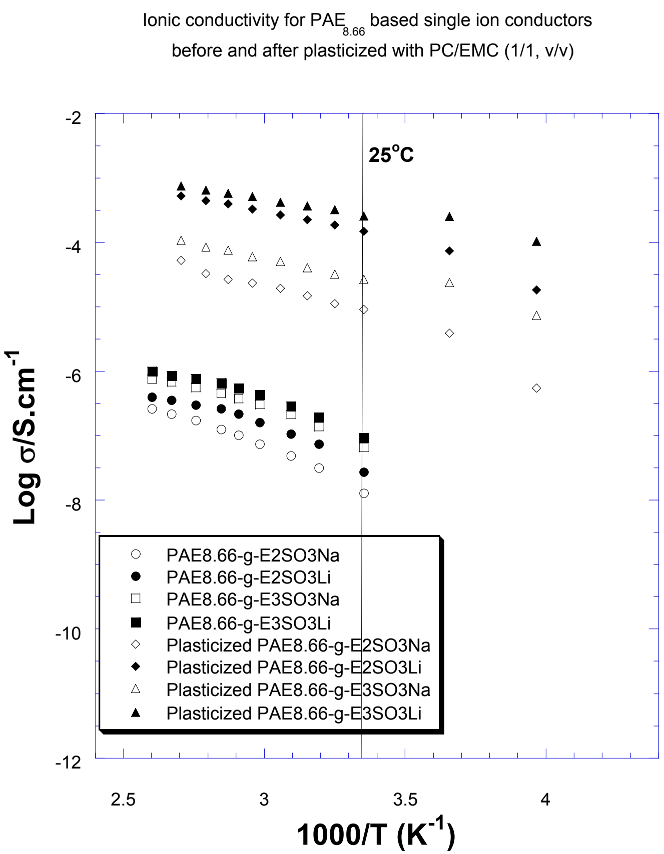
R805 – Octyl hydrophobic groups

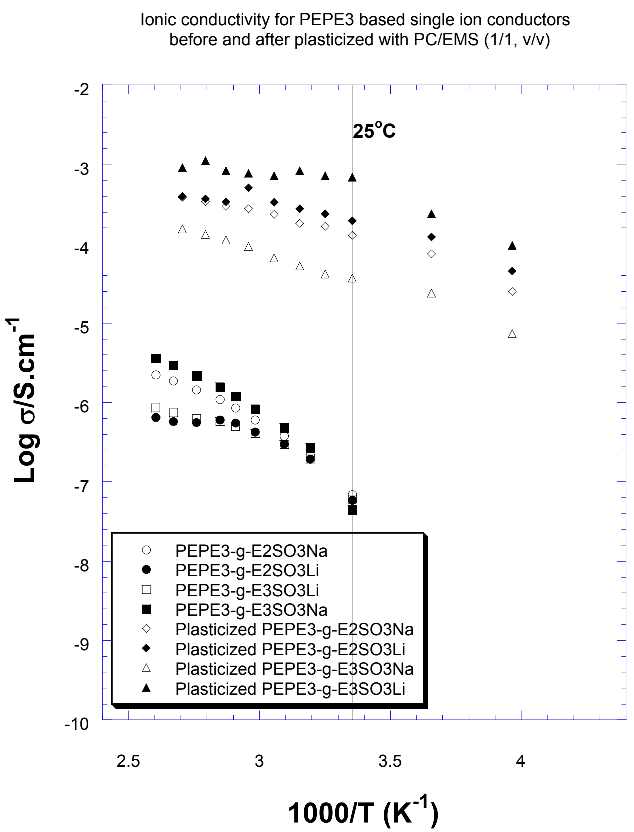




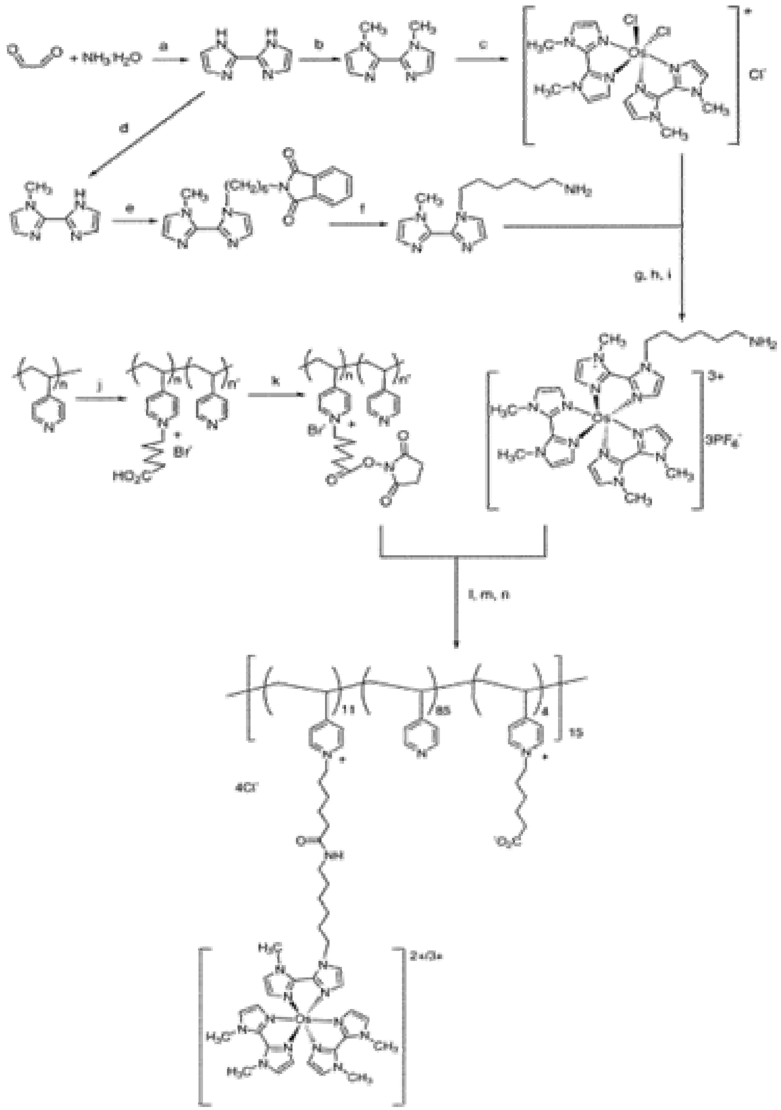
$PEPE_3$copolymer with 20% AGE-LiTFSI (20:1). X-linked to 10% density.
Note increase in T_g due to presence of salt (cf. X-link with no salt).

Single-ion Conductor Gels.
Add solvent to increase Ion transport to Useful Levels.





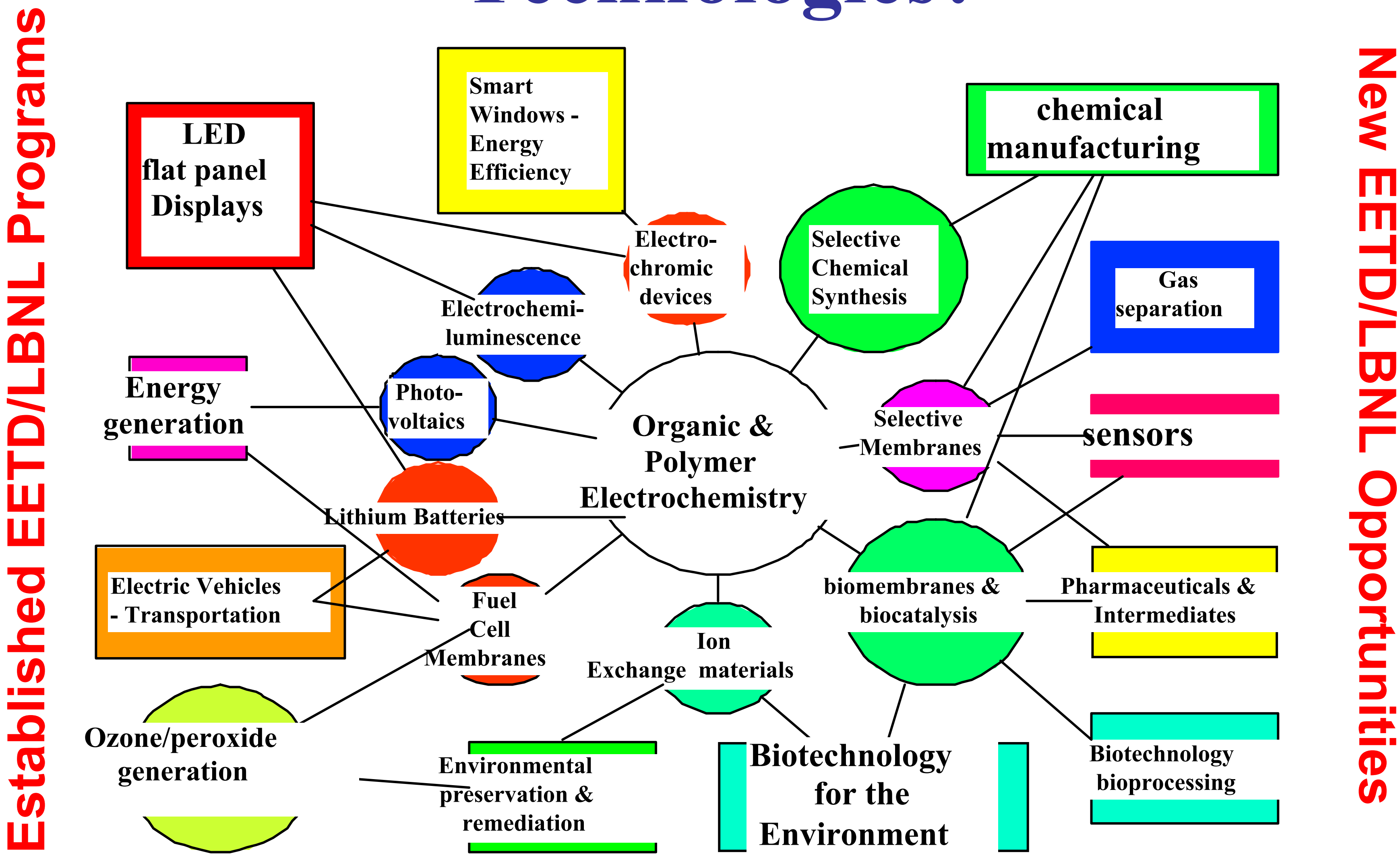
Imidazoles and Long Tethers good for Hydrogels - Heller



Imidazole provides stability
and faster kinetics.
Long tether provides faster diffusion
and leads to order of magnitude
Increas in current.

Hydrogels used for bionsensors,
medical applications, etc.

New Opportunities for Old Technologies?



Next Steps

- Prepare polyelectrolyte acid forms (usually from Na^+ form)
- Measure "dry" conductivity, T_g-values and mechanical properties.
- Dope with imidazole, pyridine and water.
  - Measure conductivity, T_g and rheology.
- Examine polymer stability.
- Attach Imidazole to polyelectrolyte and measure properties.

Next Phase

- Optimize polyelectrolyte structure for transport
  - Concentration of imidazole, anions
  - Tether length and flexibility
  - Backbone and cross-linking
- Examine material properties with carbon filler for potential MEA construction.
- Develop more stability data.
- Initiate development of structure-function relationships

Acknowledgements

- DOE-LANL
- NASA PERS program (Glenn Research Center).
- DOE Office of FreedomCAR and Vehicle Technologies